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**DIFFUSION AND ELECTRON
EMISSION PROPERTIES OF
DUPLEX REFRACTORY METAL
THERMIONIC EMITTERS**

by R. G. Hudson and L. Yang

Prepared by
GENERAL DYNAMICS
San Diego, Calif.
for Lewis Research Center



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**DIFFUSION AND ELECTRON EMISSION PROPERTIES OF DUPLEX
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SUMMARY

The diffusion and the electron emission properties of the rhenium-tungsten and the iridium-tungsten duplex emitter systems have been studied at 1600° to 2100°C in order to assess the usefulness of these systems in thermionic applications. The Re-W samples were prepared by depositing rhenium formed by the pyrolysis of ReCl_5 at 1000°C on one side of tungsten disks or tubing formed by the reduction of WF_6 with hydrogen at 550°C. The Ir-W samples were prepared by depositing tungsten formed by the reduction of WF_6 with hydrogen at 550°C on iridium disks of powder metallurgy origin and 99.99% purity. Gross diffusion-anneal was carried out in a high-temperature resistance furnace, and the rates of growth of the various phases in the diffusion zones of these systems were measured by metallographic and electron microprobe techniques and compared with the results of other workers. The electron emission properties of these systems were followed as a function of time during diffusion-anneal in a diffusion-emission cell designed for this purpose. In addition, the effective electron work functions of the same types of tungsten, rhenium, and iridium as those used in the present experiments were measured in the temperature range 1700° to 1800°C to provide reference data.

In the temperature range of thermionic interest (1600° to 1800°C), appreciable interdiffusion occurs between the components of both these systems. On the basis of the data obtained and assuming that the thickness of a diffusion layer increases with the square root of the time of diffusion, it is shown that for the Re-W system the total width of the σ phase and the χ phase formed is 6 mils at 1600°C and 12 mils at 1800°C, and the total width of the diffusion zone (defined as the region between 2 wt-% Re and 98 wt-% Re) is 14 mils at 1600°C and 25 mils at 1800°C after 10,000 hr of operation. Similar evaluations of the Ir-W system show that the width of the ϵ phase is 10 mils at 1600°C and 18 mils at 1800°C, and the total width of the diffusion zone (defined as the region between 2 wt-% Ir and 98 wt-% Ir) is 12 mils at 1600°C and 24 mils at 1800°C after 10,000 hr of operation. The vacuum emission results indicate that even when the tungsten concentration near the rhenium and the iridium emitting surfaces is negligible, the work function is lower than that of the rhenium or the iridium reference sample, presumably due to the adsorption of tungsten atoms arriving at the emitting surface by surface or volume diffusion. These observations, plus the fact that voids and cracks have been found in some of the intermediate phases formed, seen to indicate that the usefulness of the duplex emitters is rather limited.

INTRODUCTION

In the thermionic conversion of fission heat to electrical energy, refractory metals in contact with fissile materials are used in a cesium vapor environment as electron emitters. For some of the promising emitter materials, however, direct contact with nuclear fuel materials is ruled out for compatibility reasons. For instance, rhenium reacts with 80 UC-20 ZrC* and 30 UC-70 ZrC at 1600°C in 100 hr, and iridium reacts with 80 UC-20 ZrC, 30 UC-70 ZrC, and UO₂ at 1600°C in 50 to 100 hr.⁽¹⁾ A proposed solution to this problem involves the use of a duplex structure in which the emitter material is separated from the nuclear fuel by a layer of tungsten; the latter has been shown to be compatible with UC-ZrC and UO₂ at 1800°C.⁽¹⁾ The purpose of the present study was to evaluate the feasibility of the Re-W and the Ir-W duplex emitter systems on the basis of the rates of interdiffusion and the effect of such interdiffusion on the electron emission properties of these systems.

The information available in the literature on the interdiffusion of the Re-W and the Ir-W systems is summarized in Table 1. It can be seen that the results available are limited and show disagreement for the Re-W system. Even for the more thoroughly investigated Ir-W system, it was desirable to carry out independent experiments to check the reproducibility of the data. In addition, no study had been made of the electron emission properties of Re and Ir in contact with W at high temperatures.

EXPERIMENTAL TECHNIQUES

Two types of experiments were performed: (1) gross interdiffusion experiments in which the rate of interpenetration of the components of the couple is determined as a function of temperature, and (2) diffusion-emission experiments in which the electron emission characteristics of the Re and the Ir emitters in contact with W substrates are followed as a function of time at high temperatures in vacuum. The Re-W couples were prepared by depositing Re formed by the pyrolysis of ReCl₅ at 1000°C on one side of W disks or tubing formed by the reduction of WF₆ with H₂ at

* All the compositions are in mol-%.

Table 1
AVAILABLE DIFFUSION INFORMATION FOR THE Re-W AND THE Ir-W SYSTEMS

Diffusion System	Temp. Range (°C)	Diffusion Time (hr)	Composition Range	Method for Determining Penetration Curve	Essential Results	Reference
Re-W	1700	4	0-100 wt-% Re	Microhardness	Thickness of σ phase plus χ phase equals $5\ \mu$	2
	1800	3	0-100 wt-% Re	Microhardness	Thickness of σ phase plus χ phase equals $10\ \mu$	2
	1900	60	0-100 wt-% Re	Microhardness	Thickness x of intermediate phases varies with time t according to the relation $x = (kt)^{1/n}$, k and n being constants for each intermediate phase, with $n = 3.3$ for the σ phase and 1.4 for the χ phase	2
Re-W	2000	Up to 600	0-100 wt-% Re	Microhardness	Both σ and χ phases grow according to the square-root-of-time law	3
Ir-W	1700	4	0-100 wt-% Ir	Microhardness	Thickness of ϵ phase equals $12\ \mu$	2
	1800	3	0-100 wt-% Ir	Microhardness	Thickness of ϵ phase equals $18\ \mu$	2
Ir-W	1300 to 2110	52 to 1750	0-100 wt-% Ir	Electron microprobe analysis	Diffusion constants given as a function of composition and temperature	4

550°C. The Ir-W couples were prepared by depositing W formed by the reduction of WF_6 with H_2 at 550°C on Ir disks of powder metallurgy origin and 99.99% purity.

In the gross interdiffusion studies, the samples were diffusion-annealed at the desired temperature in a high-temperature resistance furnace in a vacuum of 10^{-6} torr for the planned duration. The temperature of the furnace was measured with a calibrated micro-optical pyrometer and controlled to $\pm 15^\circ C$ during the diffusion-anneal. After completion of the experiment, the samples were mounted and polished. The distribution of the concentrations of the components across the interface of the couple and the microstructures of the interface were then determined by electron microprobe analysis and metallographic techniques.

In the diffusion-emission studies, the samples were placed in a diffusion-emission cell (Fig. 1) and heated by electron bombardment of the tungsten side of the couple in high vacuum ($\sim 10^{-8}$ torr residual gas pressure) maintained with a Vac-Ion pump. The electron emission characteristics of the Re and the Ir surfaces were followed by measuring the current-voltage relationship of the emitter-collector system as a function of time up to ~ 1000 hr. The temperature of the sample was maintained to $\pm 10^\circ C$, as determined by sighting a calibrated micro-optical pyrometer into a hohlraum (10 mil diameter and 50 mil depth) drilled into the sample at about 10 mils below the emitting surface. After completion of the experiment, the sample was mounted and polished. The distribution of the concentrations of the components across the interface of the couple and the microstructures of the interface were then determined by electron microprobe analysis and metallographic techniques. To establish references for the vacuum electron emission data, the vacuum emission characteristics of a vapor-deposited W sample, a vapor-deposited Re sample, and an Ir sample of powder metallurgy origin were also studied. These reference sample materials were the same as those used in the gross interdiffusion and the diffusion-emission experiments.

EXPERIMENTAL RESULTS

The characteristics of the samples studied and the experimental conditions for each of these samples are summarized in Table 2. The results obtained with these samples are described in this section.

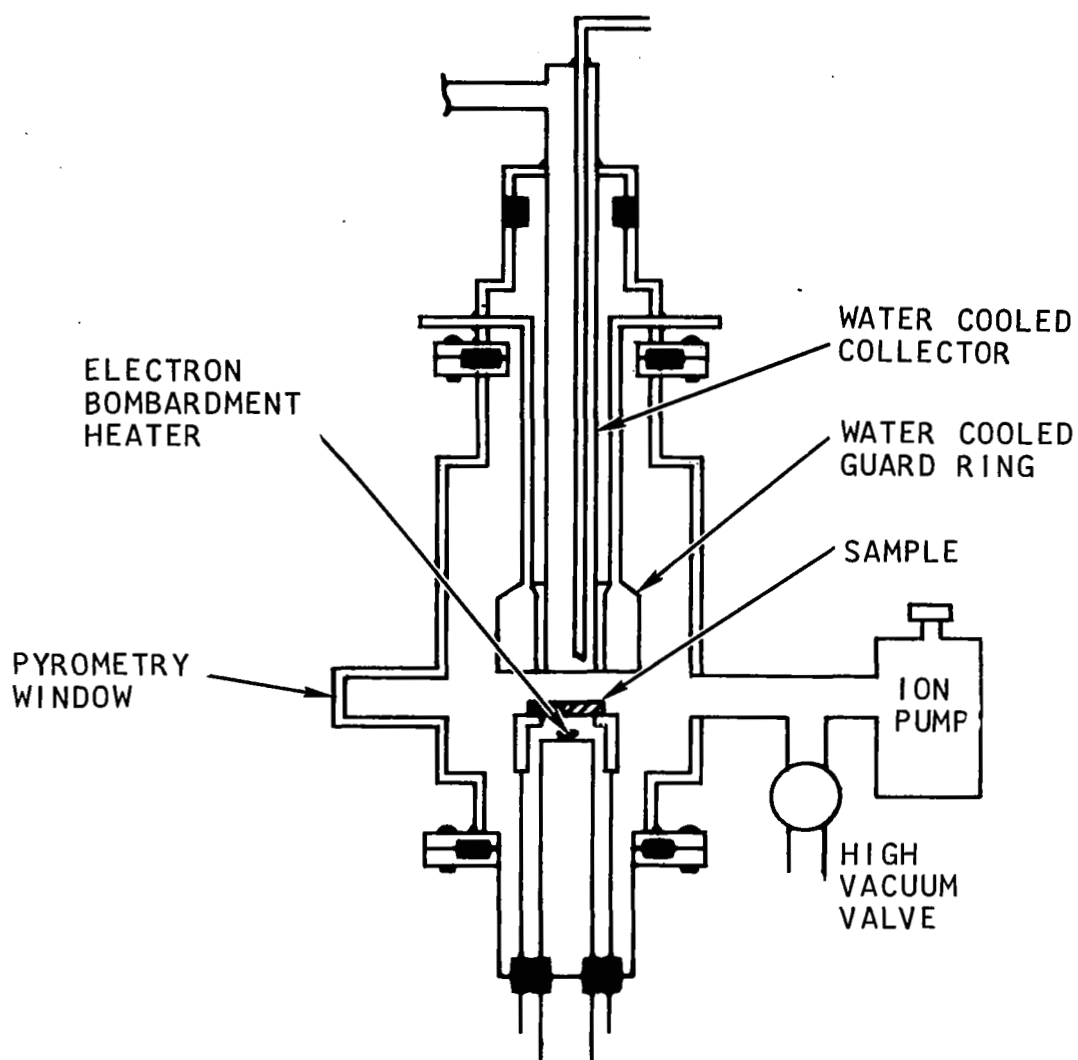


Fig. 1--Schematic arrangements in diffusion-emission cell

Table 2
CONFIGURATION AND EXPERIMENTAL CONDITIONS FOR SAMPLES STUDIED

Sample Number	Composition	Sample Configuration	Diffusion Temperature (°C)	Diffusion Time (hr)	Experiment Performed
1	Re-W	Vapor-deposited Re (20 mils thick) over vapor-deposited	2100	100	Gross interdiffusion
2		W disk (30 mils thick, 1/4 in. diameter)	2000	100	Gross interdiffusion
3	Re-W	Vapor-deposited Re (30 mils thick) over vapor-deposited W tube (100 mil wall thickness, 3/8 in. diameter)	1800	100	Gross interdiffusion
4	Re-W	Vapor-deposited Re (10 mils thick) over vapor-deposited W disk (28 mils thick, 0.614 in. diameter)	1800	1010	Diffusion-emission
5	Re-W	Vapor-deposited Re (8 mils thick) over vapor-deposited W disk (30 mils thick, 0.614 in. diameter)	1600	1006	Diffusion-emission
6	Ir-W	Ir disk (20 mils thick, 1/4 in. diameter) coated on one side with 30 mils vapor-deposited W	2100	100	Gross interdiffusion
7			2000	100	Gross interdiffusion
8			1800	100	Gross interdiffusion
9	Ir-W	Ir disk (18 mils thick, 0.560 in. diameter) coated on one side with 30 mils vapor-deposited W	1820	1011	Diffusion-emission
10	Ir-W	Ir disk (18 mils thick, 0.584 in. diameter) coated on one side with 28 mils vapor-deposited W	1600	1011	Diffusion-emission
11	W	Vapor-deposited W disk (62 mils thick, 0.570 in. diameter)	----	----	Vacuum emission reference
12	Re	Vapor-deposited Re disk (40 mils thick, 0.580 in. diameter)	----	----	Vacuum emission reference
13	Ir	Ir disk of powder metallurgy origin (40 mils thick, 0.580 in. diameter)	----	----	Vacuum emission reference

INTERDIFFUSION

Re-W System

As required by the Re-W phase relationship, ⁽⁵⁾ both the σ and χ intermediate phases are present between the terminal phases α (the Re phase) and β (the W phase) in samples studied at 1600°, 1800°, and 2000°C, and only the σ intermediate phase is present between the terminal α and β phases in the sample studied at 2100°C. Typical microstructures of the interface of the samples after the diffusion-anneal are shown in Fig. 2 for sample No. 4 which was studied at 1800°C for 1010 hr. The width of the diffusion zone, defined arbitrarily as that between 2 wt-% Re and 98 wt-% Re, and the widths of the intermediate phases σ and χ were measured from the concentration penetration curves determined by electron microprobe analysis and are summarized in Table 3.

Table 3

OBSERVED DIFFUSION ZONE AND INTERMEDIATE PHASE WIDTHS
OF Re-W DIFFUSION SAMPLES

Sample Number	Temp. (°C)	Diffusion Time (hr)	Total Width of Diffusion Zone (microns)	Width of Intermediate Phases in Diffusion Zone (microns)	
				χ	σ
5	1600	1006	113	25	22
4	1800	1010	200	25	70
3	1800	100	<u>a</u>	8	22
2	2000	100	<u>100</u>	7.5	30
1	2100	100	120	<u>b</u>	50

^aNot determined.

^bNot present.

Comparison of the data for sample No. 3 with data for sample No. 4 indicates that the widths of the intermediate phases formed increase with the square root of the time of diffusion. The same conclusion was reached by Kirner on the basis of his work at 2000°C. ⁽³⁾

Ir-W System

In agreement with the phase relationship of the Ir-W system, ⁽⁵⁾ both the σ and the ϵ intermediate phases are present between the terminal phases α (the W phase) and β (the Ir phase) in samples studied at 1820°, 2000°, and

χ phase [
 σ phase]



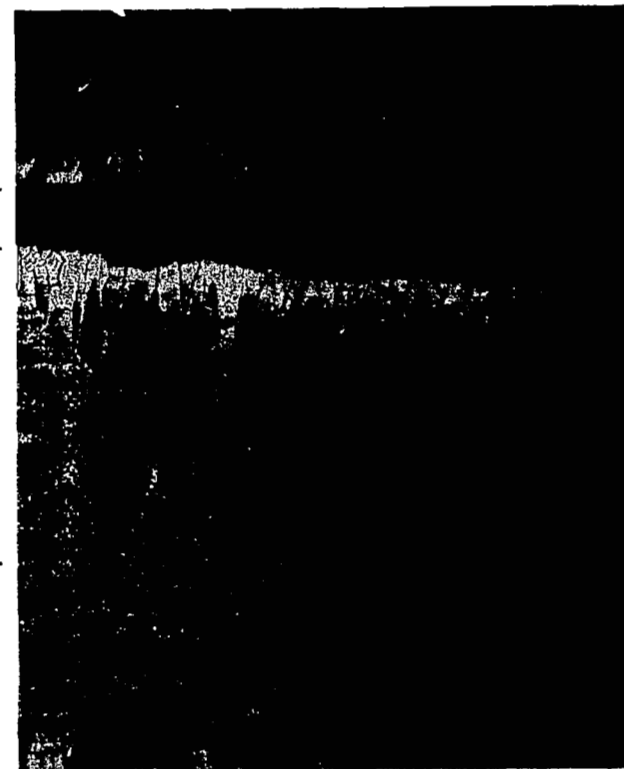
M8452-4

(100 \times)

(a) Lightly etched

— Rhenium —
 (α phase)
 [Intermediate
 phases]

— Tungsten —
 (β phase)



M8452-5

(100 \times)

(b) Heavily etched

Fig. 2--Cross section view of the Re-W interface of sample No. 4 after 1010 hr at 1800°C.
Note the presence of cracks and voids in the two intermediate phases

2100°C, and only the ϵ intermediate phase is present between the terminal α and β phases in the samples studied at 1600°C and 1800°C. Typical microstructures of the interface of the samples after the diffusion-anneal are shown in Fig. 3 for sample No. 9, which was studied at 1820°C for 1011 hr. The width of the diffusion zone, defined arbitrarily as that between 2 wt-% Ir and 98 wt-% Ir, and the widths of the intermediate phases σ and ϵ were measured from the concentration penetration curves determined by electron microprobe analysis and are summarized in Table 4.

Table 4

OBSERVED DIFFUSION ZONE AND INTERMEDIATE PHASE WIDTHS
OF Ir-W DIFFUSION SAMPLES

Sample Number	Temp. (°C)	Diffusion Time (hr)	Total Width of Diffusion Zone (microns)	Width of Intermediate Phases in Diffusion Zone (microns)	
				ϵ	σ
10	1600	1011	96	80	$\frac{a}{a}$
8	1800	100	$\frac{b}{b}$	45.5	$\frac{a}{a}$
9	1820	1011	230	166	17
7	2000	100	94	56	16
6	2100	100	132	62	18

$\frac{a}{a}$ Not present.

$\frac{b}{b}$ Not determined.

Comparison of the data for sample No. 7 with data obtained at 2025°C in Ref. 4 (ϵ = 40 microns and σ = 10 microns in 63 hours) indicates that the widths of the intermediate phases formed are approximately proportional to the square root of the diffusion time if the small difference in diffusion temperature ($\sim 25^\circ\text{C}$) is neglected. The data for sample No. 8 and the data obtained at 1800°C in Ref. 4, however, do not seem to fit this relationship. Further experimental check is needed to clarify this point.

ELECTRON EMISSION CHARACTERISTICS

W, Re, and Ir Reference Samples

In order to set reference lines for the vacuum electron emission characteristics of the Re-W and the Ir-W duplex emitters, measurements were made on the vacuum emission of individual W, Re, and Ir samples in the diffusion-emission cell at a vacuum of $\sim 10^{-8}$ torr. The materials

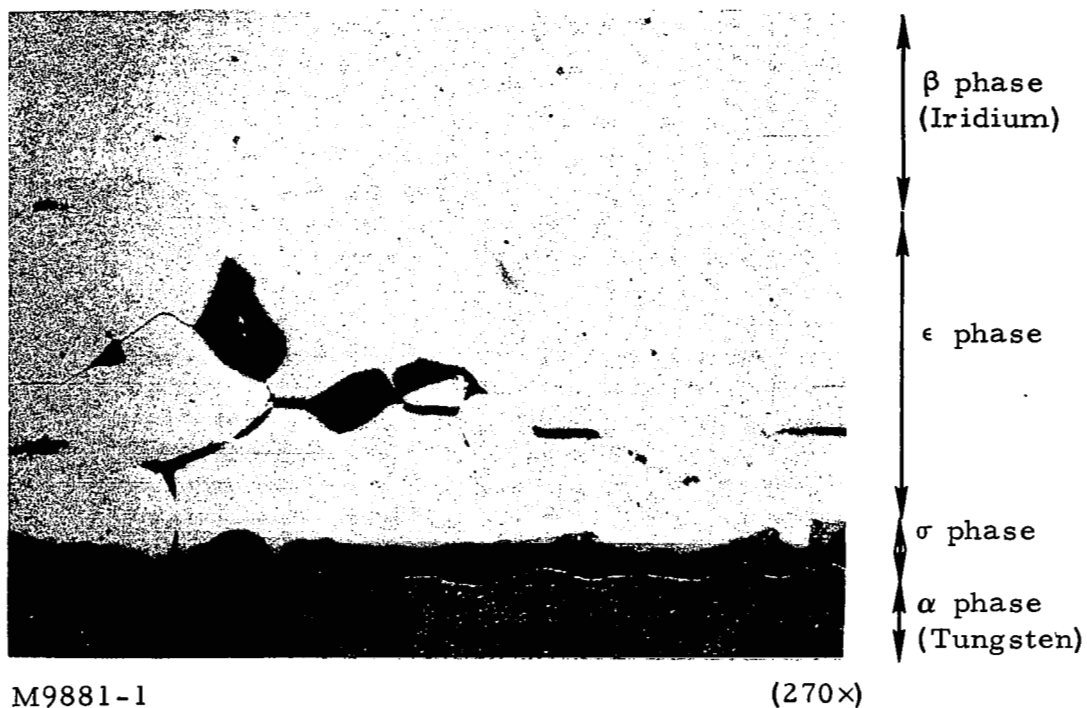


Fig. 3--Cross-section view of the Ir-W interface of Sample No. 9 after 1011 hr at 1820°C. Note the presence of large voids and some cracks in the intermediate phase ϵ

used were similar to those contained in the Re-W and the Ir-W diffusion couples. From the saturation emission current at zero field, the effective work function (ϕ) was calculated from the Richardson-Dushman equation, using a pre-exponential factor of $120 \text{ amp/cm}^2 \text{ } ^\circ\text{K}^2$. The values obtained from the Schottky plots (Figs. 4 through 6) are 4.56 eV (1716°C) and 4.55 eV (1802°C) for W (sample No. 11); 5.10 eV (1700°C), 5.11 eV (1750°C), and 5.12 eV (1800°C) for Re (sample No. 12); and 5.13 eV (1700°C), 5.15 eV (1750°C), and 5.17 eV (1800°C) for Ir (sample No. 13). Before the vacuum emission studies, the W sample exhibited strong $\{100\}$ orientation, whereas the Re and Ir samples showed no preferred orientation. The grain size of both the W sample and the Ir sample was ~ 40 microns, while the grain size of the vapor-deposited Re was extremely small (~ 5 microns). After the vacuum emission studies, there was no change in the structure of the W sample, but the Re and Ir samples both exhibited large grains (approximately a few hundred microns) and developed strong $\{0001\}$ and $\{111\}$ orientations, respectively.

Re-W Samples

The first Re-W duplex emitter sample (No. 4) was studied at 1800°C for a period of 1010 hr. The sample was prepared by depositing Re formed by the pyrolysis of ReCl_5 at 1000°C onto one side of a vapor-deposited W disk. The finished sample after polishing had a Re layer of 10 mil thickness. X-ray examination showed the normal hexagonal close-packed structure with no preferred crystal orientation. Metallographic study indicated that the grain size of the Re deposit was very small (~ 5 microns). Figure 7 shows the log current density versus square root of field plots obtained from the Re surface during the diffusion-anneal at 1800°C . The emission remained fairly steady after 434 hr at temperature. The saturation emission of 2.1 ma/cm^2 at zero field, however, corresponds to an effective work function of 4.67 eV, as compared with about 5.1 eV for the Re reference sample and 4.6 eV for the W reference sample. The microstructure of the Re surface after the vacuum emission study is shown in Fig. 8. The grain size increased from ~ 5 microns to a few hundred microns. X-ray examination showed a strong $\{0001\}$ preferred orientation.

The second Re-W duplex emitter sample (No. 5) was studied at 1600°C for a period of 1006 hr. This sample was prepared in the same manner as sample No. 4 and had the same physical characteristics. The finished sample after polishing had a Re layer of 8 mil thickness. The emission characteristics of this sample became very steady after about 200 hr at 1600°C , as shown in the log current density versus square root of field plots in Fig. 9. The saturation emission at zero field was 0.06 ma/cm^2 , corresponding to an effective work function of 4.78 eV, as compared with 5.1 eV for the Re reference sample and 4.6 eV for the W reference sample. Metallographic and X-ray studies made after the emission measurements showed that the

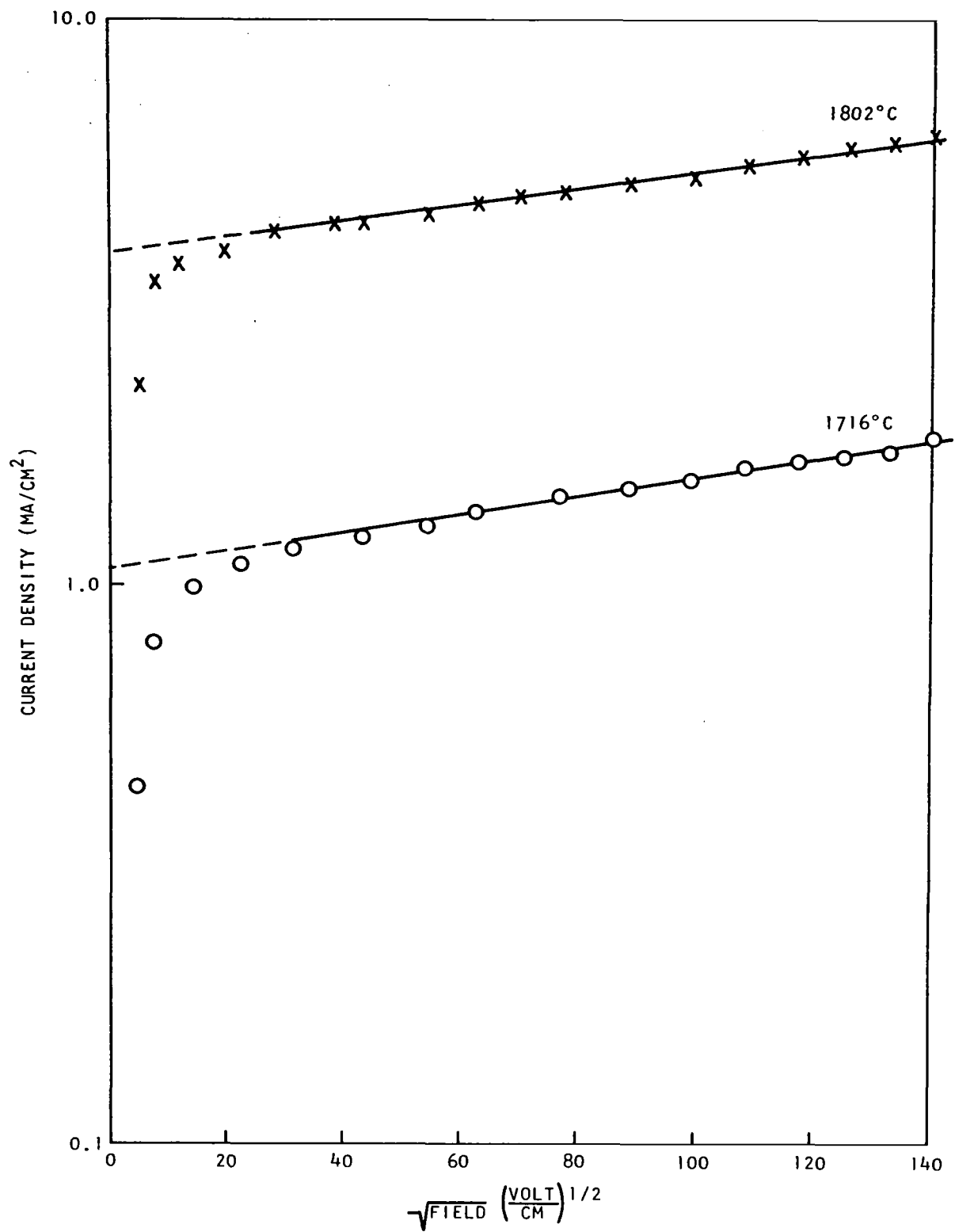


Fig. 4--Current density versus square root of field at 1716°C and 1802°C for tungsten sample No. 11

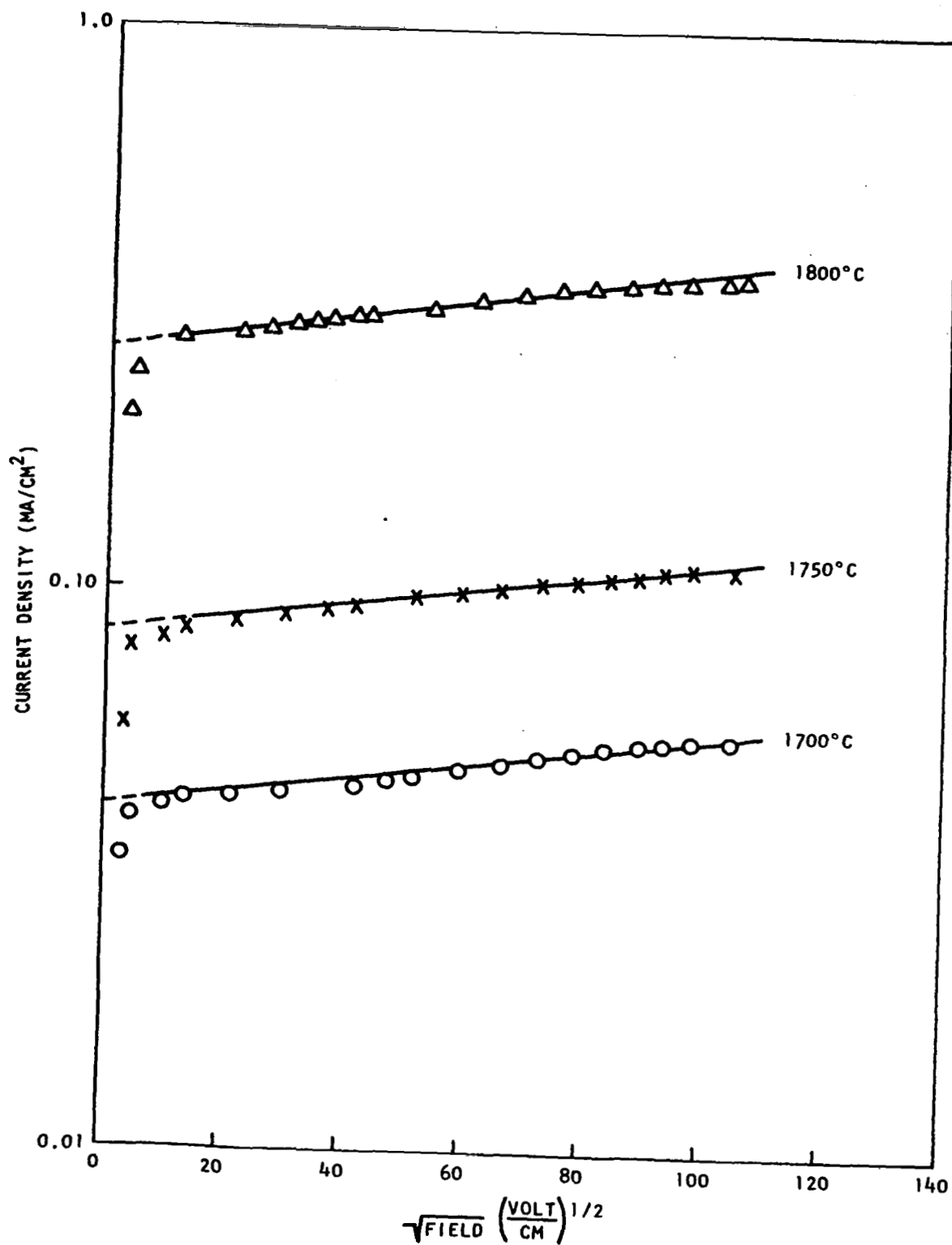


Fig. 5--Current density versus square root of field at 1700°, 1750°, and 1800°C for rhenium sample No. 12

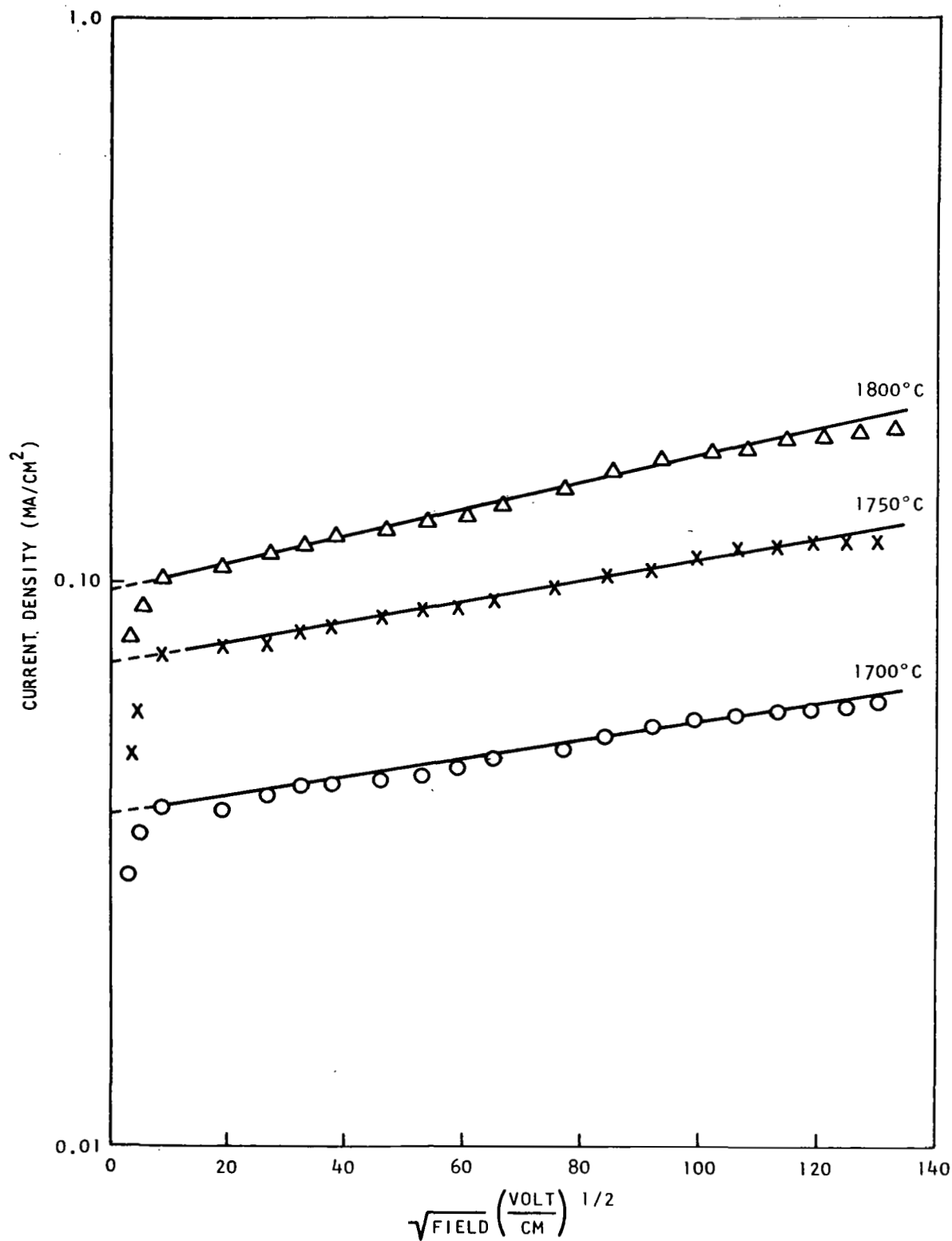


Fig. 6--Current density versus square root of field at 1700°, 1750°, and 1800°C for iridium sample No. 13

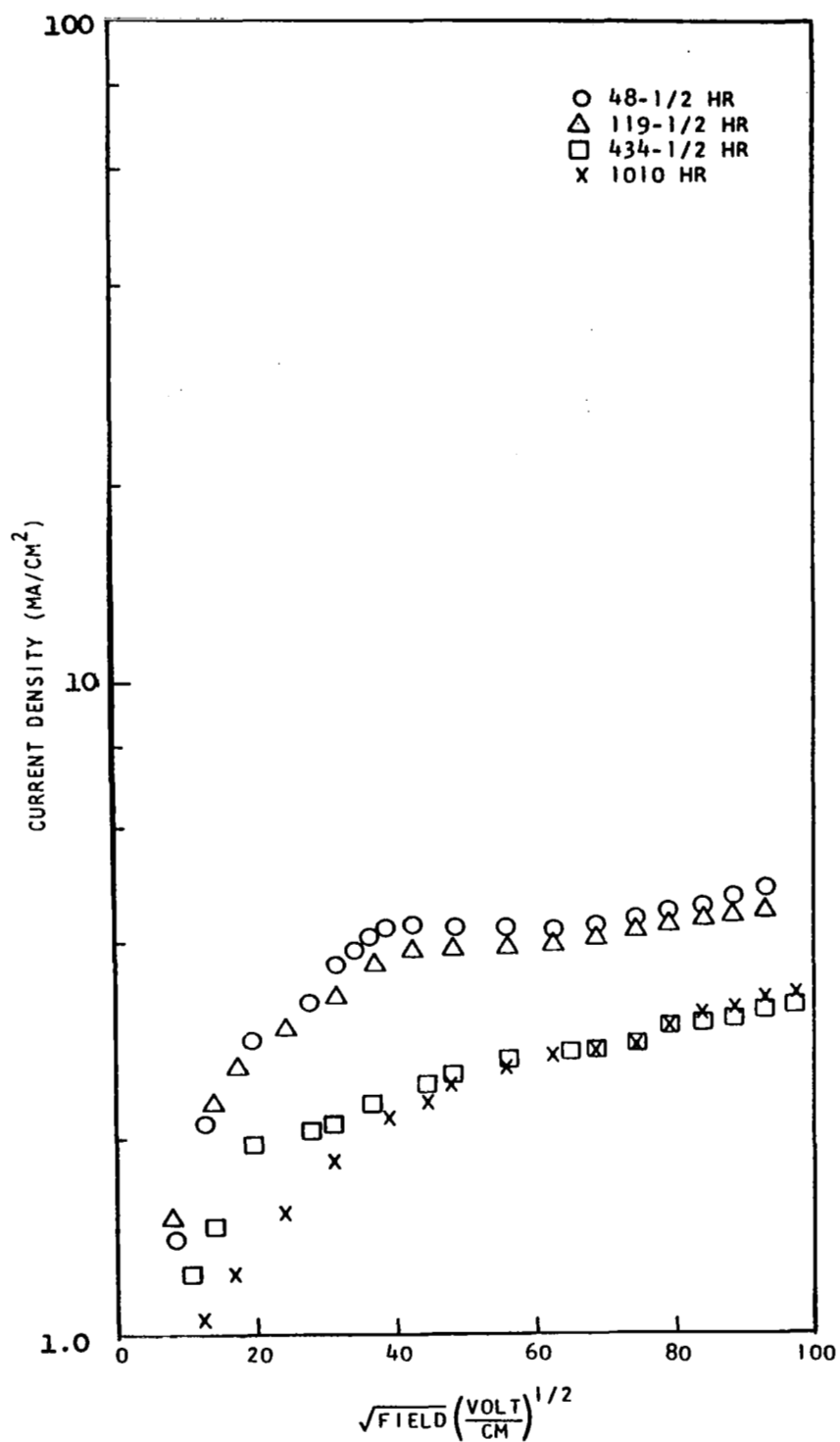
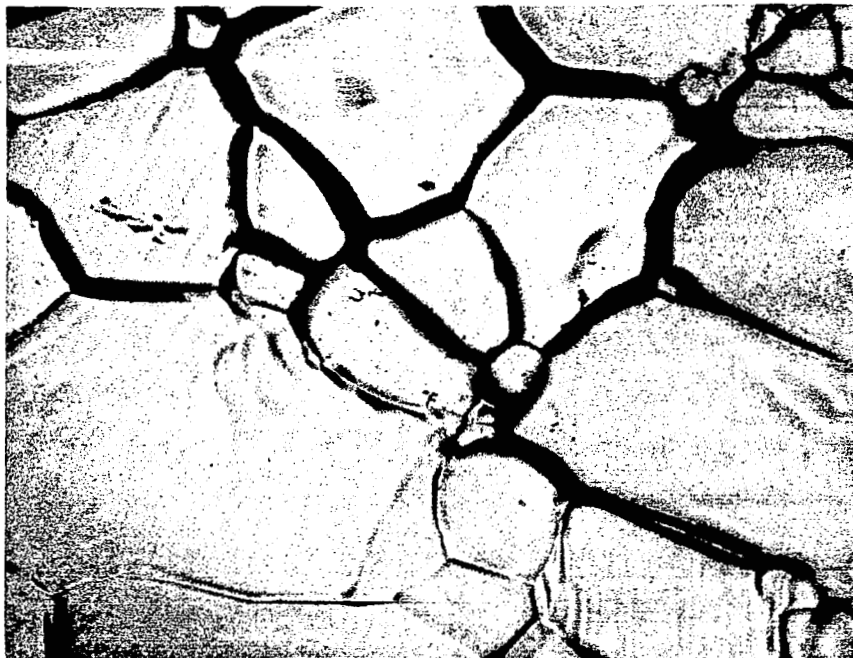


Fig. 7--Log current density versus square root of field at 1800°C and various times for Re-W duplex emission-diffusion sample No. 4



M8415

(250x)

Fig. 8--Top view of the Re surface of Re-W duplex emission-diffusion sample No. 4 after 1010 hr at 1800°C. Note the large grain size

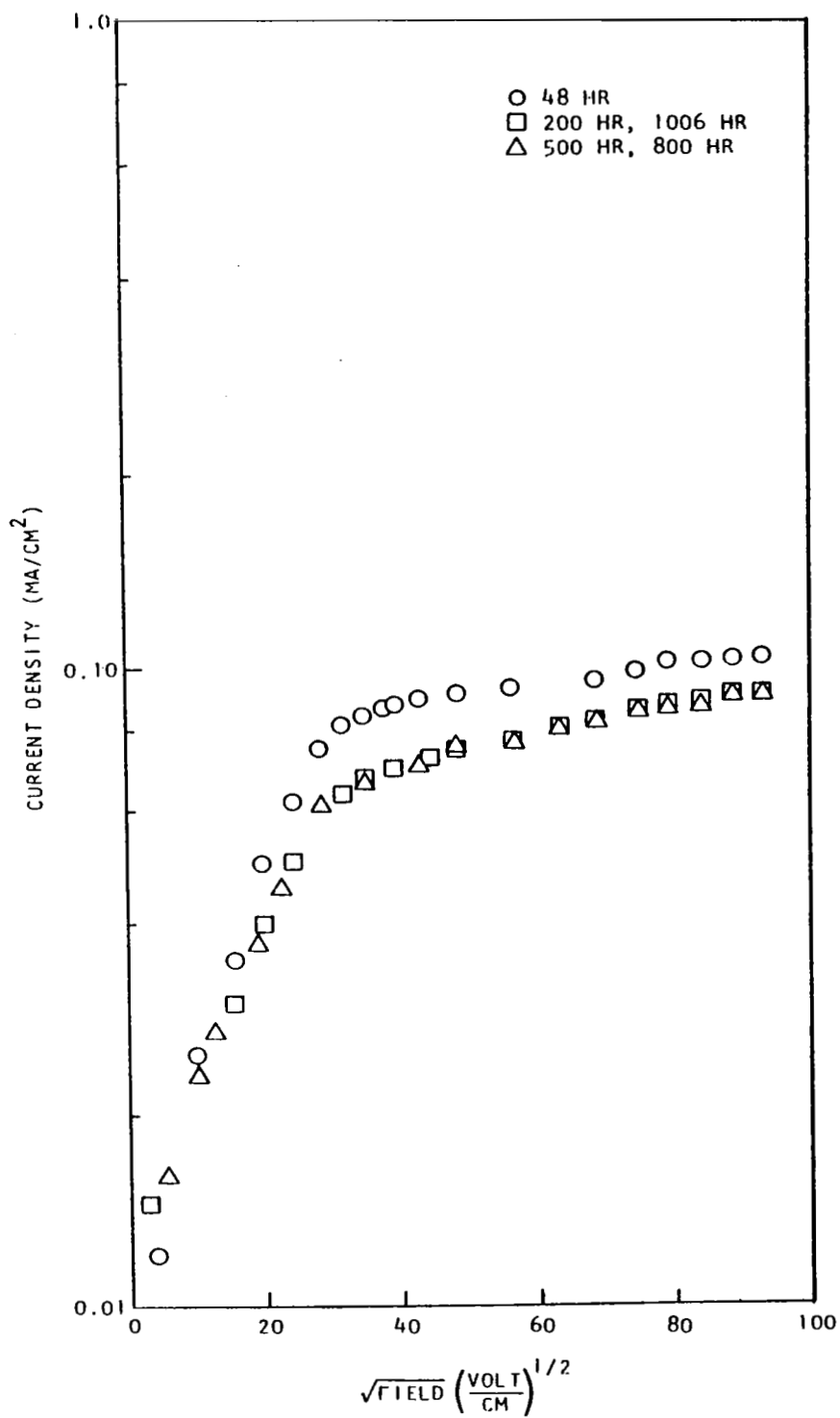


Fig. 9--Log current density versus square root of field at 1600°C and various times for Re-W emission-diffusion sample No. 5

Re grains had grown to ~75 micron size and had developed a strong {0001} preferred orientation.

The widths of the diffusion zones and the intermediate σ and χ phases in these two samples are given in Table 3. Electron-microprobe examinations indicated that the concentration of W dropped to less than 1% at a distance of about 3 mils from the Re emitting surfaces in both cases. Since the vacuum emission characteristics of an emitter are extremely sensitive to a fraction of a monolayer of impurities adsorbed on its surface, it seems likely that a small amount of W diffused to the Re surface and was adsorbed to cause the observed work function changes from that of pure Re, even though the bulk W concentration near the Re emitting surfaces may be negligible. Normally a new emitter surface needs about 100 to 200 hr for outgassing in order to stabilize its emission characteristics. The fact that neither of the Re-W duplex emitters attained the vacuum emission characteristics of pure Re seems to indicate that W adsorption on the Re surface occurred before the outgassing of either of the Re-W duplex emitters was completed.

Ir-W Samples

The first Ir-W duplex emitter sample (No. 9) was studied at 1820°C for a period of 1011 hr. It was prepared by vapor-depositing 30 mils of tungsten onto one side of an Ir disk of powder metallurgy origin and 99.99% purity. After polishing to remove surface contamination, the finished sample had an Ir layer of 18 mil thickness. The vacuum emission characteristics of this sample as a function of time at 1820°C are shown in Fig. 10. It can be seen that the emission increased continuously until it reached a steady state with a zero-field saturation emission of $\sim 3 \text{ ma/cm}^2$ after 722 hr at 1820°C, which corresponds to a work function of 4.58 ev. This is about the same value as the work function of the W reference sample. Metallographic examination of the Ir surface after the test showed very large grain size (~ 500 microns) with a considerable amount of thermal etching of the grains (Fig. 11). X-ray studies indicated a strong {111} preferred orientation.

The second Ir-W duplex emitter sample (No. 10) was studied at 1600°C for a period of 1011 hr. The sample was prepared in the same manner as sample No. 9 and had the same physical characteristics. The finished sample after polishing had an Ir layer of 18 mil thickness. The vacuum emission characteristics of this sample as a function of time at 1600°C are shown in Fig. 12. The saturation emission at zero field after the emission characteristics of the sample were stabilized after 208 hr at 1600°C was 0.09 ma/cm^2 , which corresponds to a work function of 4.71 ev. This is close to the work function of 4.6 ev for the W reference sample. Metallographic and X-ray studies indicated a grain size of ~ 250 microns,

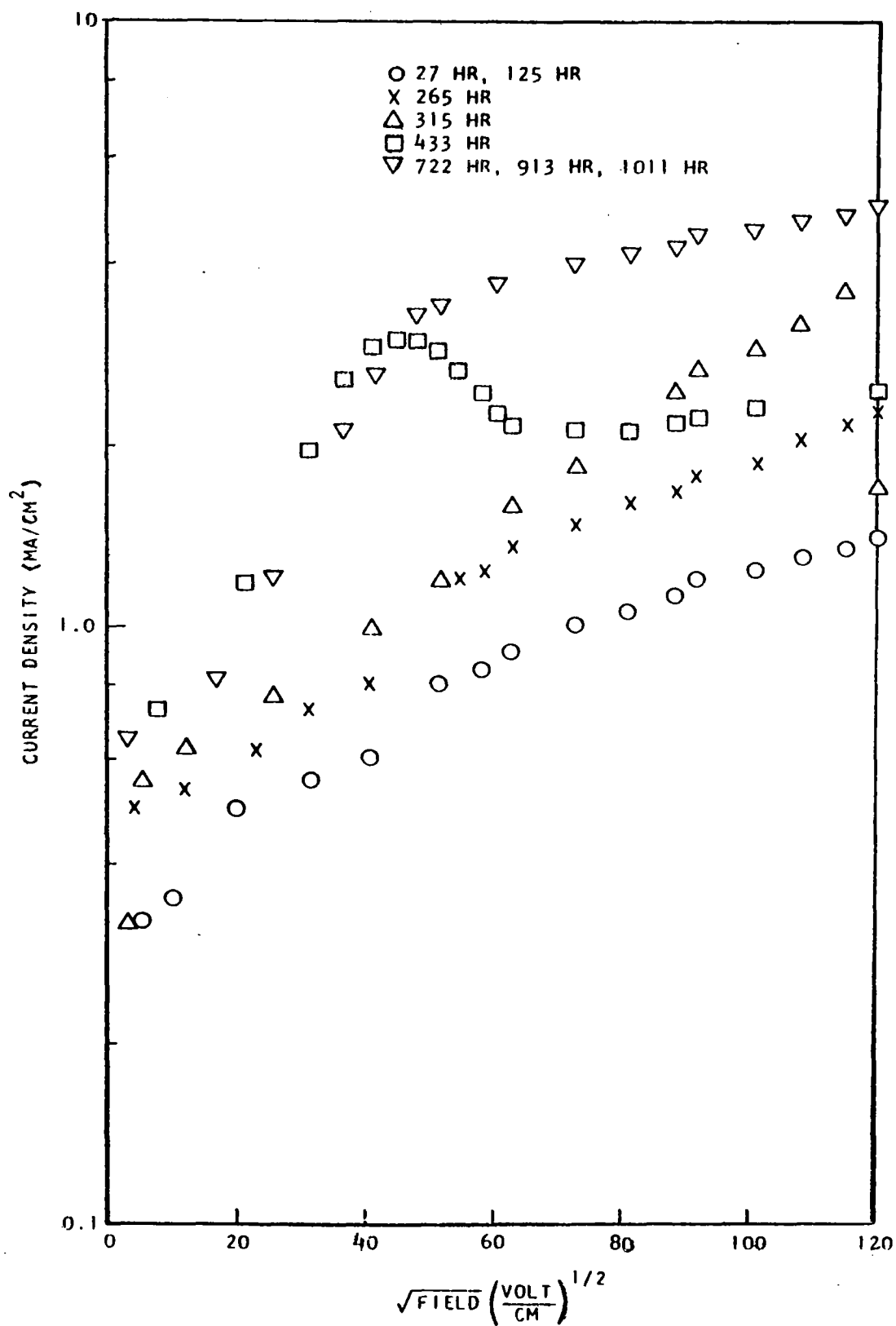
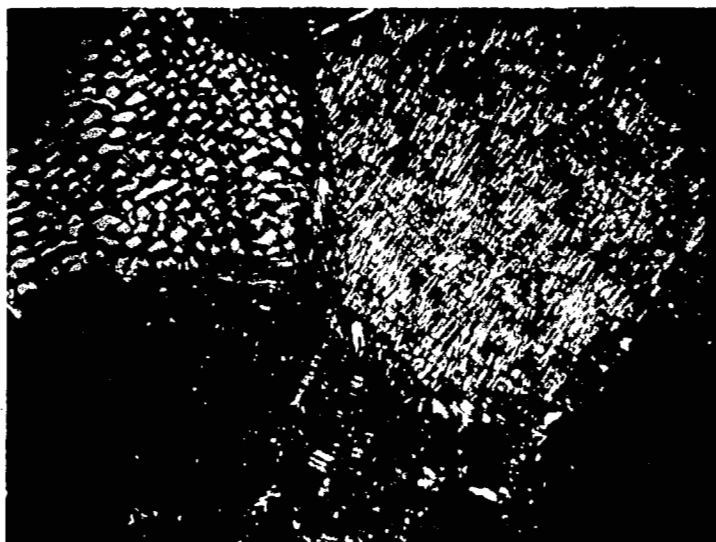


Fig. 10--Log current density versus square root of field at 1820°C and various times for Ir-W emission-diffusion sample No. 9



(100x)

Fig. 11--Top view of the iridium surface of duplex Ir-W emission-diffusion sample No. 9 after 1011 hr at 1820°C. Note the large grain size and extensive thermal etching of the grains

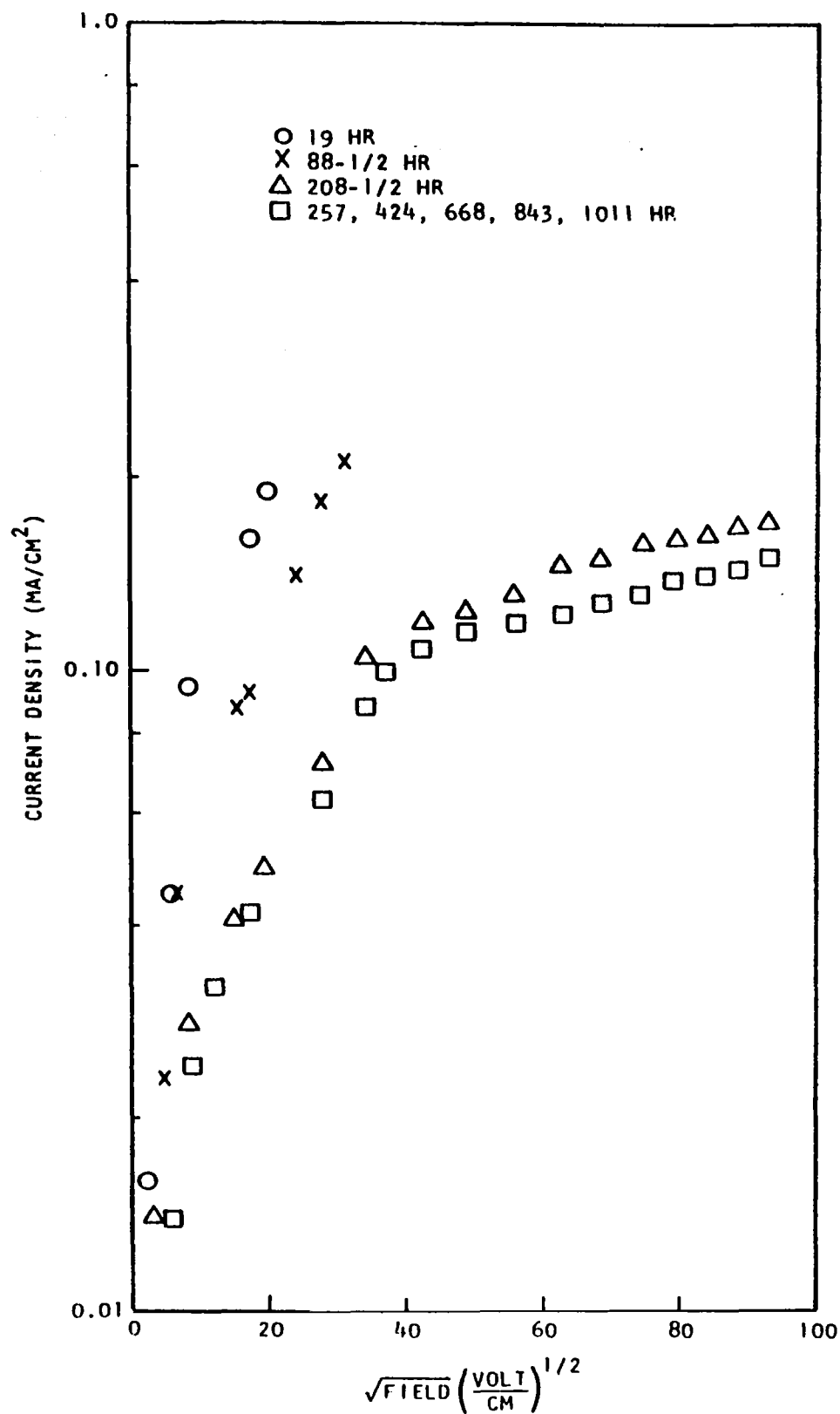


Fig. 12--Log current density versus square root of field at 1600°C and various times for Ir-W emission-diffusion sample No. 10

with evidence of thermal etching of some of the grains, and a strong {111} preferred orientation.

The widths of the diffusion zone and the intermediate ϵ and σ phases in these two samples are given in Table 4. Electron microprobe studies indicated that the concentration of W dropped to less than 1% at a distance of 7 mils from the Ir emitting surface of sample No. 9 and at a distance of 14 mils from the Ir emitting surface of sample No. 10. It is believed that the same explanation for the work function changes observed for the Re-W samples probably also applies to the Ir-W samples.

CONCLUSIONS

From the experimental results, the following conclusions can be drawn with regard to the Re-W and the Ir-W duplex emitters:

1. In the temperature range of thermionic interest (1600° to 1800° C), the Re-W system forms two intermediate phases, the χ phase and the σ phase; the Ir-W system forms one intermediate phase, the ϵ phase.
2. There is appreciable interdiffusion between the components of both these systems in the temperature range of 1600° to 1800° C during the designed operating life of these emitter systems, i. e., 10,000 hr. On the basis of the data shown in Tables 3 and 4 and assuming that the thickness of a diffusion layer increases with the square root of the time of diffusion, the widths of the diffusion zones and the intermediate phases of the Re-W and the Ir-W systems after 10,000 hr at various temperatures were calculated (Figs. 13 and 14). The data deduced from the results in Refs. 3 and 4 are also included in these figures. It can be seen that for the Re-W system, the total width of the σ phase and the χ phase is 6 mils at 1600° C and 12 mils at 1800° C; the total width of the diffusion zone is 14 mils at 1600° C and 25 mils at 1800° C. For the Ir-W system, the width of the ϵ phase is 10 mils at 1600° C and 18 mils at 1800° C, and the total width of the diffusion zone is 12 mils at 1600° C and 24 mils at 1800° C.
3. The formation of intermediate phases between the Re or the Ir emitting layer and the W substrate limits the usefulness of the duplex emitter concept for these materials. As illustrated in Figs. 2 and 3, voids and cracks may be present in these phases, especially upon thermal cycling, which impair the mechanical integrity and the heat transfer property of the duplex emitter structure.

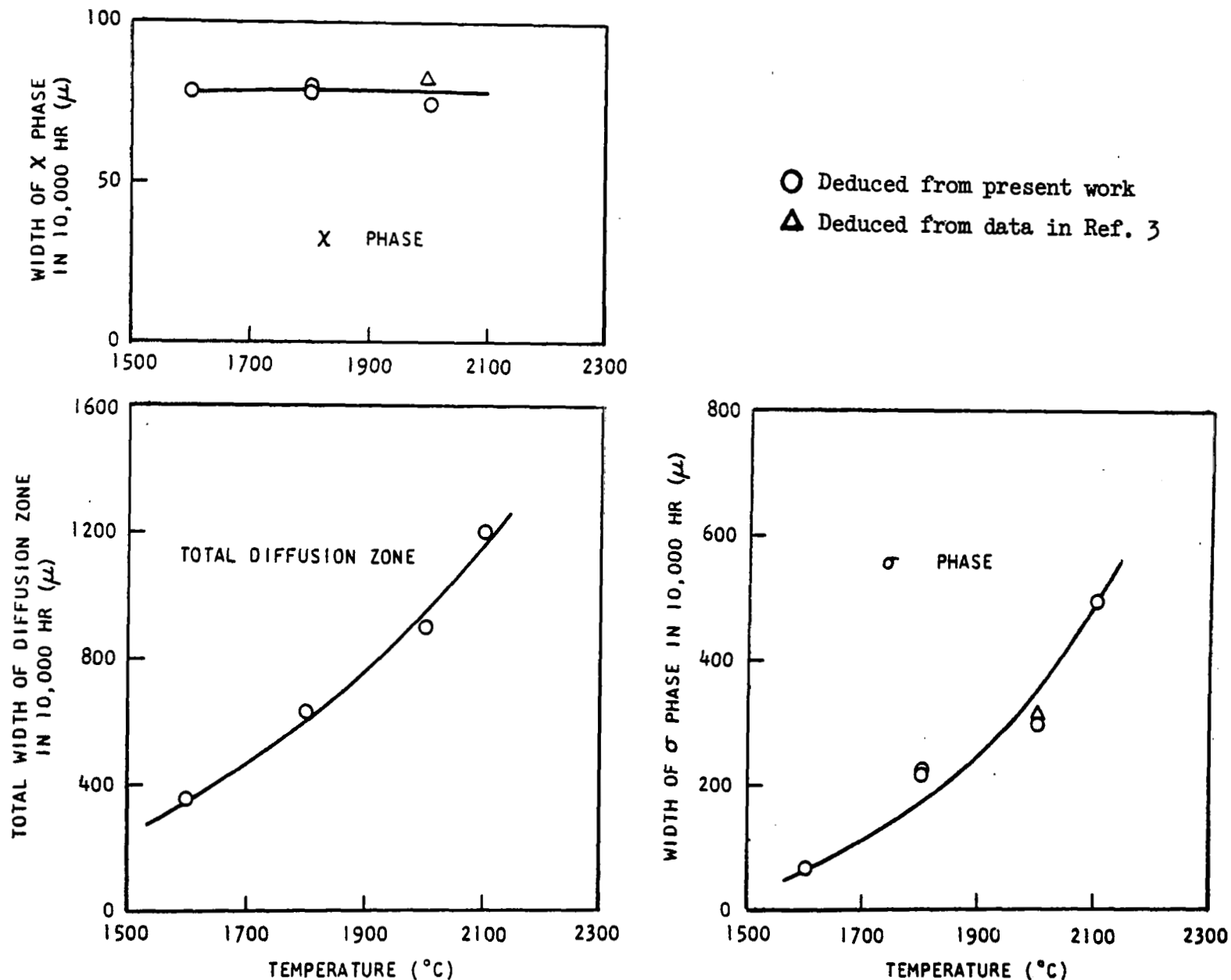


Fig. 13--Calculated width of intermediate phases and diffusion zone formed in the Re-W duplex emitter structure after 10,000 hr at various temperatures

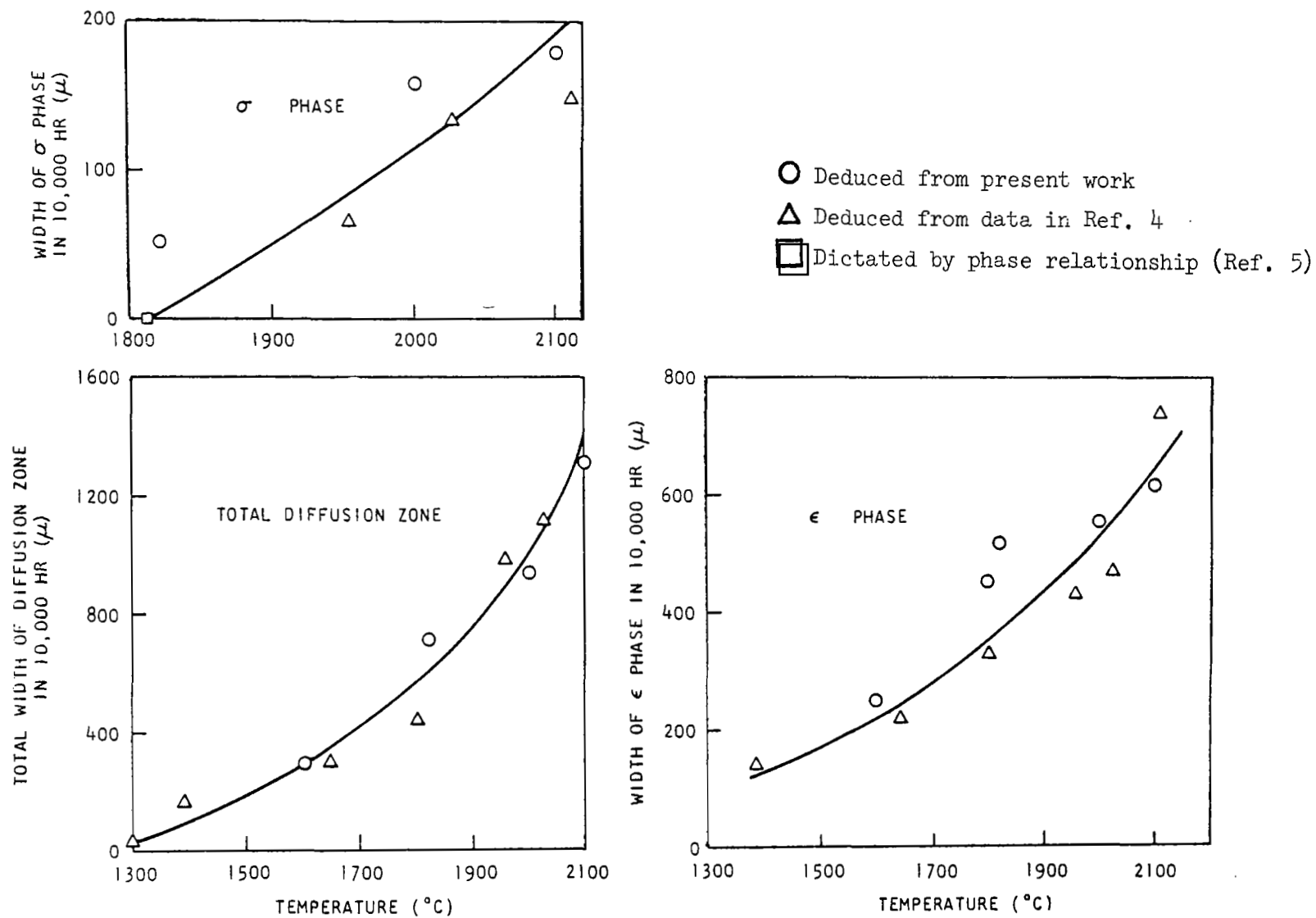


Fig. 14--Calculated width of intermediate phases and diffusion zone formed on the Ir-W duplex emitter structure after 10,000 hr at various temperatures

4. Vacuum emission studies made on the Re-W and Ir-W duplex emitters indicate that even when the W concentration near the Re or the Ir emitting surface is negligible, the work function is lower than that of the Re or the Ir reference sample. In a cesium converter, a high emitter base work function is preferred since it reduces the cesium pressure (and thus the plasma impedance loss) needed for a given emitter surface coverage by cesium atoms. Although both Re and Ir are attractive emitter materials because of their high work functions, this advantage seems to be partially lost in the samples studied in the temperature range of 1600° to 1800°C, probably due to the presence of an adsorbed layer of W on the Re or the Ir emitting surface. The samples used in these studies were prepared by depositing Re onto one side of a W disk and by depositing W onto one side of an Ir disk; part of the surface of the W substrate was therefore exposed during the experiments. The W atoms could arrive at the Re or the Ir surface by two mechanisms: (1) surface diffusion along the exposed W surface to the Re or the Ir emitting surface, or (2) volume diffusion through the bulk of the Re or the Ir layer to the emitting surface. With the present sample configuration, the contribution of each of these two mechanisms to the observed work function changes cannot be deduced individually. Nevertheless, the importance of avoiding any exposed W substrate surface is demonstrated, and this should be taken into consideration in any duplex emitter design. To study the role played by volume diffusion alone, future work using samples consisting of W completely encapsulated in Re or Ir should be carried out.

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